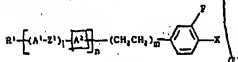


90-184497/25 E14 (25) (15) **INVER 25.11.89**
MERCK PATENT GAMBH DE 3939-116-A
 07.12.88-DE-841120 (+DE-999116) (13.04.90) C07C-255/30
 C07D-309/04 C07B-319 C07D-335/02 C07D-339 C19A-10/14
 Fluoro-benzonitrile deriv. produ. by metallation of 3-substit.
 fluoro-benzene(s), followed by carboxylation or formylation and
 conversion into nitrile
 C90-680923

(1) 3-Fluorobenzonitrile deriv. (I) of formula (I) (X = CN)
 are produced by metallation of the corresp. fluorobenzene
 deriv. (II) (X = H) to form the corresp. metal deriv. (III)
 (X = Li, Na or K), then carboxylating (III) and converting
 the carboxylic acid into (I) or formulating (III) and
 converting the resulting aldehyde into (I).



R¹ = up to 16C perfluoroalkyl, alkyl or alkynyl (opt. with
 one or more CH₂ gpps. replaced by O, S or -C≡C-)

(7-05, 10-A15B, 10-A15D) (3-D1D1)

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A¹, A² = (a) 1,4-phenylene, (b) 1,4-cyclohexylene (opt.
 with 1 or 2 non-adjacent CH₂ gpps. replaced by O
 or S) or (c) 1,4-cyclohexenylene, 1,4-bicyclo-
 [2.2.2]octylene or piperidine-1,4-diyl (with (c)
 and (b) opt. homo- or poly-substit. with H and/or Me);

Z¹ = -CH₂-CH₂-, -OCH₂-, -CH₂-O- or single bond;
 n = 0, 1 or 2; 1 m = 0 or 1; 1 + m = 1, 2, 3 or 4.
 (2) Cpd. (I) with A¹ = A² = 1,4-phenylene, Z¹ =
 -CH₂-CH₂- or single bond, 1 = n = 1, m = 0 or 1 (if m = 0,
 then Z¹ = -CH₂-CH₂-) are claimed as such.

USP/ADVANTAGES

(I) are useful as intermediates, esp. for the synthesis
 of liq. crystalline cpds., or as components of liq. crystalline
 phases (to improve dielectric anisotropy or other properties).
 The invention provides a regiospecific process for the
 prodn. of (I) in good yield.

DETAIL

(II) is, e.g. 4-R¹-3'-fluorobiphenyl, 3-fluoro-4'-R¹-
 cyclohexylbenzene, etc. (14 R¹-substit. starting cpds.)

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Noted); metallation is carried out at -80 to -50°C with, e.g.
 n-BuLi, KNH₂ etc. in a solvent such as THF, dioxane,
 cyclohexane, toluene, etc. with NMPT etc. as activator.

EXAMPLE

10 ml. 0.1-M soln. of n-BuLi in hexane was added at
 -70°C to a mixt. of 0.1 mol. 3-(trans-4-heptylcyclohexyl)-
 fluoro-benzene (prepd. as described in EP-119756) and 0.1
 mol. tetrabutylstibylendiamine in 400 ml. THF, then the
 mixt. was stirred for 3 hrs. at -70°C, treated with a mixt.
 of 0.1 mol. N-formylpiperidine and 20 ml. THF, warmed to
 room temp. and worked up to give a solid prod., 0.1 mol.
 of the aldehyde obtd. was reacted with 0.15 mol. hydroxyl-
 amine O-sulphate acid as described in Helv. Chim. Acta 59,
 2736 (1976) and worked up to give 4-(trans-4-heptylcyclo-
 hexyl)-3-fluorobenzonitrile as a colorless solid. The prod.
 had crystalline/melt transition pt., 19°C; nematic/
 isotropic transition pt., 21°C. (16pp1712DWDwgNo0/0).

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